Electrical Properties of Transparent Doped Titania Films by Sol-Gel Method (SOLID STATE CHEMISTRY-Amorphous Materials)

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Transparent semiconductive TiO_2 films co-doped with Ru and Ta (Nb), and Co and Nb (Sb) were prepared on SiO_2 glass substrates by the sol-gel method using $Ti(OC_3H_7^i)_4$ solutions. The solution preparation condition, solution composition, dopant content and heat-treatment temperature all severely affected the electrical resistivity of the resultant films. TiO_2 films co-doped with Ru and Ta (Nb) showed n-type conductivity, while those co-doped with Co and Nb (Sb) showed p-type conductivity. It seems that the obtained films can be utilized for assembling all-solid-state TiO_2-based pn type solar cell.

Keywords : Transparent semiconductive films / Sol-gel method / Titania films / Electrical resistivity / pn type solar cell

Solar energy is believed to be an essential energy source of the next century. A pn type solar cell with all-solid-state TiO_2-based films seems to have many benefits for effective utilization of the solar energy because the ultra violet and visible light of solar light would be adsorbed by n-type TiO_2 and p-type TiO_2, respectively. Here, transparent semiconductor electrodes with high conductivity are requested. We prepared TiO_2 films co-doped with Ru and Ta (Nb), and Co and Nb (Sb) by sol-gel method, aiming at making n- and p-type transparent semiconductive films, respectively. The effects of solution composition, solution preparation condition, dopant content and heat-treatment temperature on the electrical resistivity of sol-gel derived films were studied. The conduction mechanisms of doped TiO_2 films were also discussed.

Transparent semiconductive n-type TiO_2 films were prepared by co-doping Ru and Ta (Nb). Titanium tetraisopropoxide ($Ti(OC_3H_7^i)_4$), $RuCl_3 \cdot xH_2O$, $TaCl_5$ ($NbCl_5$), C_2H_5OH, 36.5% HCl (60% HNO_3 or diethanolamine (DEA)) and H_2O were used as starting materials.

Transparent semiconductive p-type TiO_2 films were obtained by co-doping Co and Nb (Sb). $Ti(OC_3H_7^i)_4$, $CoCl_2$, $NbCl_5$ ($SbCl_5$), C_2H_5OH, acetylacetone (AcAc), (36.5% HCl) and H_2O were used to form $Ti_{3(1-x)}Co_xM_{2x}O_6$ (x = 0.3, M = Nb or Sb) solid solutions.

The gel films were dip-coated on SiO_2 glass substrates at a constant rate of 1 cm/min, heat-treated in air at 400°C-900°C for 10 min. Repeating the above procedure 3 times gave approximately 120 nm-thick films.

D.C. electrical resistivity was measured in air at room temperature for n-type TiO_2 films and during cooling from high temperature to room temperature for p-type TiO_2 films with two electrodes method.

The obtained n-type TiO_2 films were uniform and transparent in all the preperation conditions employed, and their crystalline phases were anatase when HCl or

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Scope of research

Inorganic amorphous materials with various functions are the targets of research in this laboratory. (1) To obtain a clear view of "what is glass" and the bases for designing functional glasses, we investigate the structure of glasses using X-ray and neutron diffraction analysis, high resolution MAS-NMR, and ab initio MO calculation. (2) To develop materials of high optical nonlinearity, we search heavy metal oxide-based glasses and transition metal oxide thin films, and evaluate the nonlinear optical properties by Z-scan methods. (3) Using sol-gel method, synthesis and microstructure control are carried out on various functional oxide thin films.

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HNO_3 was used as a catalyst. The resistivity of the films decreased in the order of DEA > HNO_3 > HCl additives. Refluxing the dopant solutions prior to mixing with $Ti(OC_3H_7^i)_4$ solution led to the decrease of the film resistivity. This was probably caused by the alkoxylation of $RuCl_3$ and $TaCl_5$ under refluxing, promoting the formation of solid solution.

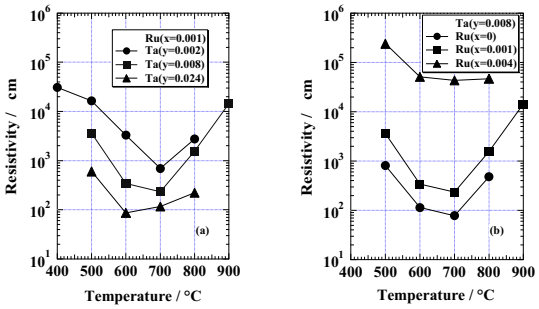

Figure 1. (a) Electrical resistivity of the titania films with a fixed content of Ru (x = 0.001) and various contents of Ta (y = 0 - 0.024). (b) Electrical resistivity of titania films derived with various Ru contents (x = 0 - 0.004) and a fixed Ta content (y = 0.008).

Figure 1 shows that the resistivity decreased with increasing Ta content and increased with increasing Ru content. This indicates that Ti^{3+} species, which are formed by Ta-doping via charge compensation, are the main donors responsible for the conduction in the present anatase samples (see Figure 2). Moreover, most of the films showed resistivity minima at a heat-treatment temperature of 700°C. This is due to the change of Ti^{3+} concentration by the Ta incorporation and the oxidation and reduction reactions during the heat-treatment. The lowest resistivity of $10^1 \sim 10^2$ Ω cm was attained.

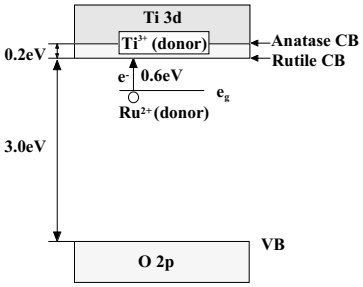

Figure 2. Schematic energy level diagram for Ti^{3+} and Ru^{2+} in anatase and rutile TiO_2.

The obtained p-type TiO_2 films were also uniform and transparent when AcAc was used, while samples heat-treated at 800°C became opaque when HCl was added. Rutile phases appeared when the films were heat-treated at 700°C. Films co-doped with Co and Sb changed their crystalline phases from amorphous directly to rutile with increasing heat-treatment temperature. Contrarily, films co-doped with Co and Nb showed phase transition from anatase to rutile on heating. The crystallinity of films co-doped with Co and Nb was slightly better than that of films co-doped with Co and Sb.

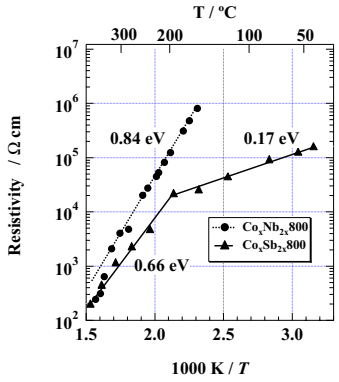

Figure 3. Variation of logarithmic resistivity with reciprocal temperature in K for $Ti_{3(1-x)}Co_xM_{2x}O_6$ (M = Sb or Nb) films heat-treated at 800°C. The inserted numericals in eV are activiation energies.

Figure 3 shows that logarithmic resistivity of films co-doped with Co and Nb was directly proportional to the reciprocal absolute temperature. On the other hand, the slopes for films co-doped with Co and Sb were different below and above 200°-220°C, indicating that there are at least two conduction mechanisms with different activation energies. The phenomenon should be closely related to the valence state of Sb ions, causing the formation of different acceptor levels. Moreover, Co ion in $Ti_{3(1-x)}Co_xM_{2x}O_6$ may be present as Co^{2+} in high spin state, acting as an acceptor for electrons from the valence band of TiO_2. (see Figure 4).

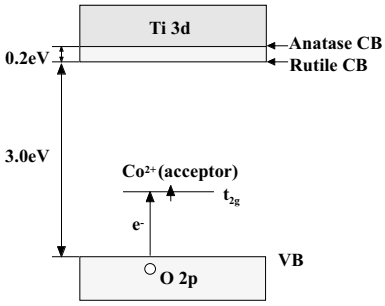

Figure 4. Schematic energy level diagram for high spin Co^{2+} in titania.

The above obtained transparent n- and p-type TiO_2-based semiconductors are promising materials for designing a pn type solar cell.

References

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